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INHOMOGENEITY AND MESOSTRUCTURE OF OXIDE COATING ON GLASS

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Inhomogeneity (in depth) of Ti, Al, and Zr oxide coatings deposited on glass using a sol-gel method is attributed both to the effect of the mesostructure of oxide components and to quantum transfer of waveguide light. Substantial deviation from the additivity of the refractive index is observed for $TiO_2 - ZrO_2$ coatings. Homogeneity in depth and RI additivity can be attained if one of the components is present in excess.

The increasing demand for optical coatings necessitates adoption of efficient methods of inhomogeneity control of the coatings in depth. Spectroscopy and ellipsometry enable determination of the average optical density and thus it appears difficult to control the parameters of deposition and composition of a complex compound. When using physicochemical methods, including etching, control of inhomogeneity of coatings is accompanied by their degradation or damage to a certain area of the coating.

Of particular interest is a nondestructive waveguide control of optical coatings consisting of the determination of the film inhomogeneity in depth and the presence of mesostructure fragments responsible for quantum transfer of the waveguide light using the change in refractive index. Different methods of control are developed [1 – 4] to determine the parameters of the layers of complex composition on the glass surface obtained through ion-exchange, electrodiffusion, microalloying, and also through evaporation of batches of complex composition in vacuum. The possibility of changing the inhomogeneity of the refractive index (RI) in depth for oxide and nonoxide coatings obtained by the sol-gel method is established. The goal of this study is to improve the procedure for determining the RI inhomogeneity [3, 4] in depth with allowance for the effect of mesostructure of oxide coatings obtained by sol-gel method on glass articles.

We considered $TiO_2 - SiO_2$, $TiO_2 - Al_2O_3$, and $TiO_2 - ZrO_2$ coatings obtained upon centrifugation of solutions of Ti, Si, Al, and Zr isopropylates of given compositions with their subsequent drying at 80 – 100°C and firing at 200 – 450°C. Monitoring is performed on a unit consisting of a LGN-104 laser, a G-5 goniometer, and an attachment for clamping a GaP ($n_3 = 3.85$) prism to the coating. If the gap between the prism and the coating is small (Fig. 1), the exponentially decaying wave field of the prism enters the layer, thus exciting waves in the coating. The matching condition for phase constants is of the form

$$\beta_m = (2\pi n_3 / \lambda) \sin \theta_m ,$$

where n_3 is the refractive index of the prism, $\lambda = 0.63$ μm is the wavelength of incoming light, and θ_m is the entrance angle of wave m.

The values of the effective RI of the waves propagating in the coating are determined from the following expression:

$$n_m = n_3 \sin [\alpha + \arcsin (\sin \theta_m / n_3)],$$

where α is the angle at the prism base.

Positioning of θ_m is performed by the maximum of the energy brought into the coating. Then the intensity of the ray reflected from the prism base is measured.

Coatings of different thickness (from 0.5 to 2.0 μm), different distribution of the refractive index in depth, and different deviation from the law of additivity of refractive contributions to the refractive index (which holds true for solid compounds, see Table 1) were obtained upon different heat treatment regimes and at different concentrations of TiO_2 ad-

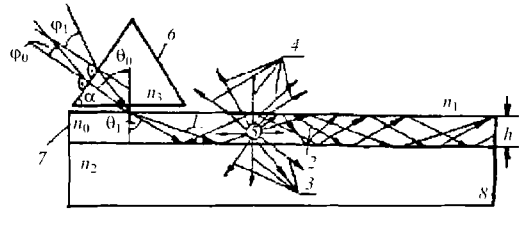

Fig. 1. Scheme of waveguide light distribution in the coating: *1* and *2*) substrate waves (*3*) with $m = 0$ and 1, respectively; *4*) radiative waves; *5*) inhomogeneity; *6*) prism; *7*) coating; *8*) substrate.

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TABLE 1

Coating parameters	Oxide additive in the solution, % (molar content)														
	SiO_2					Al_2O_3					ZrO_2				
	10	50	60	70	100	20	30	50	60	100	20	40	60	80	100
RI	1.92	1.70	1.65	1.57	1.52	1.88	1.80	1.75	1.66	1.60	1.88	1.79	1.74	1.74	2.03
Deviation from additivity, %	0	52	68	71	–	14	26	45	60	–	12	30	40	68	

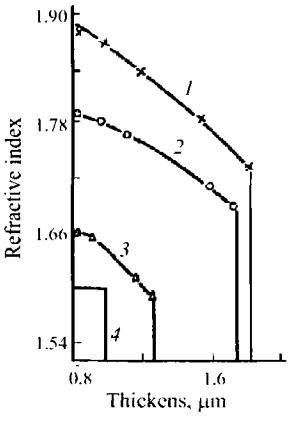

Fig. 2. Profiles of the RI distribution in TiO_2 Al_2O_3 coatings. Molar content in Al_2O_3 solutions: *1*) 20%, *2*) 30%, *3*) 60%, and *4*) 100%.

ditives. Thorough mixing of Ti isopropylates with isopropylates of the corresponding additive ensures formation of solutions which are homogeneous in composition. It can be seen (Table 1) that as the content of additives increases, the deviation from additivity also increases whereas the homogeneity of coatings in depth decreases to the minimum only if one of the oxides is in excess. For $TiO_2 - SiO_2$ and $TiO_2 - Al_2O_3$ coatings the best additivity of refractive oxides is attained at annealing temperatures of 350 and 450°C, respectively.

$TiO_2 - SiO_2$ coatings having a molar content of TiO_2 up to 50% exhibit RI values that match the model of gradual (stepped) RI distribution and minimum inhomogeneity in depth. At a low content of SiO_2 the spectra of effective RI exhibit a linear dependence on the mode number and parabolic distribution of RI in depth. When the content of SiO_2 exceeds 15% $n_2 \rightarrow n_1$ and the conditions of waveguide light propagation in the coating are thus disturbed. Optical homogeneity of $TiO_2 - Al_2O_3$ coatings in depth is attained at a content of Al_2O_3 up to 30% and above 60%. When the content of Al_2O_3 ranges from 30 to 60% the RI profile in depth exhibits a parabolic form (Fig. 2). A substantial deviation from the additivity is observed in $TiO_2 - ZrO_2$ coatings. Long-term annealing at a temperature above 450°C results in enlarging of grains from 15 to 90 nm.

Chemical homogeneity of the solutions used in sol-gel technology and thorough mixing of the additives introduced have no visible effect on the inhomogeneity of coatings in depth. The inadequacy thus observed is attributed to formation of a mesostructure which ensures quantum transfer of polarized waveguide light. The resulting RI profile of the coating depends on scaled coordination of 2D electron lattices approximating the grain mesostructure. When the number of lattices is rather large the contribution to waveguide propagation due to quantum transfer also becomes rather large and the mode structure of a smooth function of RI of the coating is observed. If waveguide light propagates under one of these lattices and the other structure of the coating does not match the condition of quasiperiodicity of RI, then the RI profile may be step-shaped. As the thickness of coatings increases, the mesostructure with oxide layering at the boundaries of the layers loses its properties. They totally disappear as the volume of the material participating in waveguide light propagation increases.

Thus, the inhomogeneity of the coatings obtained on glass articles by the sol-gel method is attributed to the nature of oxide additives and to the mesostructure of nanograins. This is observed upon monitoring of oxide coatings using waveguide propagation of polarized light. A substantial effect of the mesostructure and oxide layering on the refractive index is observed in thin coatings.

The method of determinating the inhomogeneity of oxide coatings on glass articles can also be applied to other materials.

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